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Title of Invention : Rubber Hose Reinforcing Cord

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Specification

1. Title of Invention
Rubber hose reinforcing cord.

2. Claims of the Patent

(1) Rubber hose reinforcing cord which is characterized as follows : In the rubber hose reinforcing cord, the fiber which forms the said cord is the sheath core type composite fiber in which the polyethylene -2,6- naphthalate in which ethylene naphthalatene -2,6 - dicarboxylate is the main component is the core component and the material in which polyamide is the main component is the sheath component around the said core component ; ratio of the core component which forms the said composite fiber is 30 ~ 90 weight % and the strength of said cmoposite fiber is over 7.0 g/d and elongation is below 20 % ; initial tensile resistance is over 90 g/d and dry heat shrinkage is below 5 % and the said composite fiber is twisted to make the cord.

(2) The rubber hose reinforcing cord which is characterized as follows : In Claim (1), for the polyethylene -2,6 - naphthalate which forms the core comonent of composite fiber, the limiting viscosity [η] is over 0.5, the birefringence is 230 x 10^{-3} ~ 350 x 10^{-3}, density is over 1.340 g/cm^3 ; for the polyamide which forms the sheath component, the sulfuric acid relative viscoisty (η_r) is over 2.8, birefringence is over 45 x 10^{-3}, density is over 1.135 g/cm^3 ; both of the said core component and sheath component have

the fiber structure of high orientation and high crystallinity.

3. Detailed Description of the Invention

[Field of Application in Industry]

This invention is related to the rubber hose reinforcing cord. Specifically, it is related to the rubber hose reinforcing cord consisting of the sheath core type composite fiber in which polyethylene - 2,6- naphthalate (hereinafter, this is called 2,6-PEN) is the main component of the core component and polyamide is the main component of the sheath component.

[Existing Technology]

As the hose reinforced with the cord consisting of polyester fiber in which polyethylene terephthalate is the main repeating unit, for example, Kokai JP No. 159882 - 1987 describes one.

[The Problem Which the Invention Intends to Solve]

In the case of rubber hose in which the rubber reinforcing cord made of polyester fiber is used as the reinforcing material as described in the said Kokai JP No. 159882 - 1987, the hose has excellent dimensional stability and is used effectively as the hose for water conveyance. However, with the increase in the pressure of working fluid which has occurred with the increase in the performance of fluid machines, there occurs the fatigue of polyester fibers and the separation of rubber and polyester fibers and the hose is damaged in a relatively short time. The said damage occurs particularly often in the case where a large fluctuation of pressure acts repeatedly on the hose and it was found to occur as the result of strong rubbing of the cords.

Objective of this invention is to eliminate the above said problem in the existing technology and to provide the rubber reinforcing cord which has particularly high modulus and undergoes small deformation even when high pressure acts on it repeatedly, also has very good heat resistance, has durability against the separation from rubber and to provide the rubber hose which is reinforced with the said rubber hose reinforcing cord.

[The Means for Solving the Problem and Action]

The constitution of this invention lies in

(1) Rubber hose reinforcing cord which is characterized as follows : In the rubber hose reinforcing cord, the fiber

which forms the said cord is the sheath core type composite fiber in which the polyethylene -2,6- naphthalate in which ethylene naphthalatene -2,6 - dicarboxylate is the main component is the core component and the material in which polyamide is the main component is the sheath component around the said core component ; ratio of the core component which forms the said composite fiber is 30 ~ 90 weight % and the strength of said cmoposite fiber is over 7.0 g/d and elongation is below 20 % ; initial tensile resistance is over 90 g/d and dry heat shrinkage is below 5 % and the said composite fiber is twisted to make the cord.

(2) The rubber hose reinforcing cord which is characterized as follows : In Claim (1), for the polyethylene -2,6 - naphthalate which forms the core comonent of composite fiber, the limiting viscosity [η] is over 0.5, the birefringence is 230 x 10^{-3} ~ 350 x 10^{-3}, density is over 1.340 g/cm^3 ; for the polyamide which forms the sheath component, the sulfuric acid relative viscoisty (η_r) is over 2.8, birefringence is over 45 x 10^{-3}, density is over 1.135 g/cm^3 ; both of the said core component and sheath component have the fiber structure of high orientation and high crystallinity.

The rubber hose reinforcing cord which is due to this invention is a composite fiber in which the core component is 2,6-PEN and the sheath component is polyamide. The said composite fiber is what could not be obtained by the existing technology and it has high modulus, in-rubber heat resistance, heat resistant adhesion and durability against the separation of polymer at the sheath core composite interface which are superior to those of polyester. These characteristic properties can be indicated by the specific combined parameters consisting of the birefringence and density of the 2,6-PEN and polyamide fiber sections which form the core and sheath, respectively.

Strength of the said composite fiber can be made to be over 7.0 g/d by having the 2,6-PEN of limiting viscosity [η] of over 0.5, preferably over 0.6, as the core component of the said composite fiber.

Like the 2,6-PEN core component, the polymer of the polyamide sheath component also needs to have a high degree of polymerization in order to obtain the composite fiber of high strength and its sulfuric acid relative viscosity is over 2.8, preferably over 3.0. In the polyamide sheath component, copper salt and other organic and inorganic compounds are added as the thermal oxidative degradation prevention agent. In particular, it is preferred to contain 30

~ 500 ppm, as copper, of the copper salt such as copper iodide, copper acetate, copper chloride, copper stearate, 0.01 ~ 0.5 weight % of the alkali metal halide such as potassium iodide, sodium iodide, potassium bromide and/or 0.01 ~ 0.1 weight % of organic, inorganic phosphorus compound.

Ratio of the 2,6-PEN core component in the said composite fiber is 30 ~ 90 wt % ; if the 2,6-PEN component is less than 30 wt %, one can not obtain the composite fiber in which the modulus and dimensional stability of the 2,6-PEN component are effectively utilized and one can not obtain good rubber hose reinforcing cord. On the other hand, if more than 90 wt % is occupied by the 2,6-PEN core component, the adhesion to rubber is poor when the said cord is used as the tensile resistant material of the rubber hose and one can not ahieve the improvement of heat resistance of the rubber hose reinforcing cord in the rubber.

In the above mentioned composite fiber, it is desirable that both of the 2,6-PEN core component and polyamide sheath component have high level of orientation and crystallization and that the birefringence of the 2,6-PEN core component is kept in the range of 30×10^{-3} ~ 350×10^{-3}. If it is less than 230×10^{-3}, strength of the composite does not reach over 7.0 g/d and initial tensile resistance does not go over 90 g/d in some cases. Also, if it exceeds 350×10^{-3}, the improvement of fatigue resistance is not achieved.

On the other hand, birefringence of the polyamide sheath component is over 45×10^{-3} and normally over 50×10^{-3} and so it is highly oriented. If the birefringence is less than 45×10^{-3}, it is difficult to obtain the composite fiber which has high strength and high initial tensile resistance.

Measurement of birefringence of the sheath core composite fiber can be conducted as follows. Measurement for the sheath section is done directly with a transmission interference microscope and the measurement of core section is done by dissolving the polyamide sheath cmponent in formic acid, sulfuric acid or fluorinated alcohol and then by using the transmission interference microscope.

As for the density, it is desirable that 6-PEN core component has a density greater than 1.340 g/cm^3 and polyamide sheath component has a density greater than 1.135 g/cm^3 and that they have high degree of crystallinity. When the densities are over the above mentioned specific values, the dimensional stability and fatigue resistance of the composite fiber are good and, when made into the rubber hose reinforcing cord and used as the tensile resistant material of rub-

ber hose, the heat resistance of the said tensile resistant material in rubber is markedly improved.

Measurement of the density of 2,6-PEN core component is done with the polyamide sheath cmoponent dissolved and removed with formic acid, sulfuric acid, fluorinated alcohol, etc and the density of the polyamide sheath component can be determined by calculation from the density of composite fiber and the density of the 2,6-PEN core section.

The composite fiber which is characterized as described above has a high strength of over 7.0 g/d and initial tensile resistance of over 90 g/d and an elongation of less than 20 %. More preferred properties of the composite fibers are strength of over 7.3 g/d, initial tensile resistance of over 100 g/d and elongation of 8 ~ 16 % and these can be achieved by combining the above described conditions properly.

The above said composite fiber is made by the novel method which is shown below.

In order to obtain the above mentioned polymer properties of the 2,6-PEN core component, the polymer which consists substantially of 2,6-PEN having a limiting viscosity [η] of over 0.5, normally over 0.6, is used.

For the polyamide sheath component, the polymer having the sulfuric acid relative viscosity of over 2.8, normally over 3.0, is used.

In the melt spinning of the said polymer, it is preferred to use 2 units of extruder type spinning machines. The 2,6-PEN and polyamide polymer which were melted by each of the extruders, respectively, are led to the composite spinning pack and this is spun through the composite spinning die into the spun composite fiber in which 2,6-PEN is positioned at the core section and polyamide is positioned at the sheath section to make the spun yarn.

The spinning speed is high at over 300 m/min. Directly underneath the said composite spinning die, there is installed the heat preserving cylinder, heated cylinder for the heated atmosphere of over 200 deg C, preferably over 260 deg C, for a distance of over 10 cm and less than 1 m. The said spun yarn is passed through the above mentioned heated atmosphere and then it is quenched and solidified by cold air ; then, it is imparted with the oiling agent and then is taken up by the take up roll which controls the spinning speed. Control of the heated atmosphere directly underneath the

said die is important for maintaining the spinnability. The undrawn yarn which was taken up is drawn continuously without winding up first.

Next, the said undrawn yarn is heat-stretched at the temperature of over 180 deg C, preferably over 200 deg C. Drawing is done in more than 2 stages, normally in more than 3 stages and the draw ratio is in the range of 2.0 ~ 6.5. Use of such high temperature drawing in this invention contributes to the improvement of durability of the composite interface. When the drawing temperature of the third stage in the said drawing is low, e.g. below 160 deg C, the interfacial separation of the 2,6-PEN core component and polyamide sheath component occurs at drawing ; also, when drawing is done below 180 deg C, the same occurs at the time of processing the rubber hose and when the rubber hose is used repeatedly under a high pressure. Also, when the draw ratio is over 6.5, deformation at drawing is large and interfacial separation occurs in some cases and, also, the fatigue resistance drops and so this is not good.

As to the method of obtaining the rubber hose by using the above said composite fiber which forms the rubber hose reinforcing cord which is due to this invention, for example, the drawn yarn obtained is twisted to make the untreated cord and the said untreated cord is treated with the adhesive agent in which resorcine, formalin and latex are the main components and, after this, heat treatment is done to make the treated cord. Then, at the outer circumference of a flexible mandrel made with resin or rubber, the inner rubber layer is extrusion-molded and then this is placed in a vulcanization can and the inner rubber layer is vulcanized or semi-vulcanized ; then, on the outer circumference of the said vulcanized or semi-vulcanized inner face rubber layer, the intermediate rubber layer is extrusion-molded ; then, at the outer circumference of the said intermediate rubber layer, the fiber reinforced layer is formed by using the treated cord consisting of the composite fiber which is due to this invention ; then, at the outer circumference of the said fiber reinforcing layer, the outer rubber layer is extrusion molded. Then the whole thing is placed in the vulcanization can again and the whole body is vulcanized.

When the fiber reinforced layer is made of 0a plural number of layers, an insulation is formed between the first fiber reinforced layer and the second fiber reinforced layer.

[Examples of Application]

Examples of Application 1 and 2, Comparative Examples 1 through 3.

Polyethylene-2,6-naphthalate (2,6-PEN) of limiting viscosity [η] 0.8 and hexamethylene adipamide (N66 : sulfuric acid relatively viscosity η_r 3.3) containing 0.02 wt % of copper iodide and 0.1 wt % of potassium iodide were melted separately by 40 o extruder type spinning machines and these were led to the composite spinning pack. From the sheath core composite spinning die, spinning was done with the 2,6-PEN at the core section and with the polyamide at the sheath section to make the composite yarn. Ratio of the core component and sheath component of the said spun yarn was varied as shown in Table 1. For the die, one with 120 holes of hole diameter 0.4 mm o was used. As to the polymer temperature, 2,6-PEN was melted at 300 deg C and polyamide was melted at 290 deg C and the spinning was done with the spinning pack temperature at 300 deg C. Directly under the die, a heated cylinder of 30 cm was attached and this was heated such that the temperature of atmosphere in the cylinder would be 290 deg C.

The atmospheric tempeature is the temperature of the atmosphere measured at the position which is 10 cm below the die face and 1 cm apart from the filament at the outermost circumferential position. Under the heated cylinder, a chimney of annular shape with a length of 400 mm was attached and, from around the yarn, cold air at 25 deg C was blown at 40 m/min perpendicularly against the yarn for cooling.

Then, the oiling agent was imparted and the yarn speed was controlled by the take up roll rotating at the speed shown in Table 1 and then, without winding up first, this was drawn continuously. Drawing was conducted in 3 stages by using 5 pairs of Nelson type rolls ; after this, 3 % relaxation was given for relaxation heat treatment and then it was wound up. As for the drawing conditions, the take up roll temperature was 60 deg C, the first draw roll temperature was 120 deg C, the second draw roll temperature was 190 deg C, the third draw roll tempeature was 225 deg C, and the tension control roll after drawing was not heated. The first stage draw ratio was 70 % of the total draw ratio and the remainder was divided into 2 stages for drawing. The spinning was conducted with the variation of extrusion rate matched to the spinning speed and draw ratio such that the denier of drawn yarn would be about 500 denier (Examples of Application 1, 2, Comparative Example 1). 3 pieces of the drawn yarn were put together to make 1500 denier.

For the yarn-making condition, properties of the drawn yarn and the fiber structure parameters, comparative tests were conducted with the polyethylene terephthalate (PET) fiber (1500-288-702C) (Comparative Example 2) and the nylon 66 fiber (1260-204-1781) (Comparative Example 3). The conditions and fiber properties were as shown in Table 1.

Table 1

TABLE 1

			C1 比較例1	E1 実施例1	E2 実施例2	C2 比較例2	C3 比較例3
1	ポリマ組成		2，6－PEN／N66	2，6－PEN／N66	2，6－PEN／N66	PET	N66
2	ポリマ組成比	（重量比）	70：30	70：30	70：30	100：0	0：100
3	紡糸速度	（m／min）	280	1000	1500	－	－
4	延伸倍率		7．2	6．1	3．2	－	－
5	複合繊維の物性						
6	繊　　度	（d）	1501	1510	1508	1502	1262
7	強　　度	（g／d）	9．9	9．0	8．3	9．5	9．6
8	伸　　度	（%）	10．0	10．1	10．1	12．0	19．8
9	初期引張り抵抗度	（g／d）	164	160	153	102	42
10	乾熱収縮率	（%）	4．0	2．0	1．5	10．1	3．5
11	2，6－PEN芯繊維物性						
12	極限粘度	（η）	0．68	0．69	0．69	（0．92）	－
13	複屈折	（×10⁻³）	358	311	298	192	－
14	密　　度	（g／cm³）	1．337	1．349	1．358	（1．391）	－
15	ポリアミド鞘繊維物性						
16	硫酸相対粘度	ηr	3．4	3．3	3．4	－	（3．2）
17	複屈折	（×10⁻³）	54．0	53．8	52．1	－	（57．3）
18	密　　度	（g／cm³）	1．140	1．145	1．149	－	（1．142）

19 注）PET芯繊維物性のうち（　）内はPET繊維物性を示し、
ポリアミド鞘繊維物性のうち（　）内はポリアミド繊維物性を示す。

C1. Comparative Example 1 ; E1. Example of Application 1

1. Polymer composition ; 2. Polymer composition ratio (wt ratio) ; 3. Spinning speed ; 4. Draw ratio ; 5. Properties of the composite fiber ; 6. Denier ; 7. Strength ; 8. Elongation ; 9. Initial tensile resistance ; 10. Dry heat shrinkage ; 11. 2,6-PEN core fiber properties ; 12. Limiting viscosity ; 13. Birefringence ; 14. Density ; 15. Polyamide sheath fiber properties ; 16. Sulfuric acid relative viscosity ; 17. Birefringence ; 18. Density ; 19. Note) Among the PET core fiber properties, ( ) indicates the PET fiber property and, among the polyamide sheath fiber properties, ( ) indicates the polyamide fiber property.

Using each of the yarns which were shown in Table 1, 1500/2 greige cord was made by applying 40T/10 cm twisting for the upper twisting and lower twisting in reverse directions, respectively. For N66 of Comparative Example 3, however, number of tiwsting was 39T/10 cm to make 1260/2 greige cord. These greige cords were made into dip cords by imparting adhesive agent and conducting heat treatment by using the dipping machine of Ritzler Co.

The dip solution contained 20 % of the adhesive component consisting of resorcine, formalin, latex and the imparting was controlled so that the adhesive component will stick by 4 %. Heat treatment was conducted at 225 deg C for 80 seconds by applying a stretch such that the intermediate elongation of the dip cord would be about 5 %. Nylon 66 was treated under the same heat treatment condition by applying a stretch such that the intermediate elongation would be about 9 %. For the PET fibers, the 2 bath adhesion treatmnet was conducted by the common method and the heat treatment was conducted at 240 deg C for 120 seconds by applying a stretch so that the intermediate elongation would be about 5 % .

With the dip cords which were made in this manner, test pieces in which the cords were buried in the rubber as in the case of using as the tensile resistant material in rubber hose were made and the in-rubber heat resistance, adhesion property and fatigue resistance were evaluated. Results were as shown in Table 2.

Table 2

TABLE 2

			C1	E1	E2	C2	C3
			比較例1	実施例1	実施例2	比較例2	比較例3
1	繊度	(d)	3534	3569	3554	3504	2755
2	強力	(kg)	24.3	23.2	22.2	21.7	21.5
3	強度	(g/d)	6.87	6.50	6.25	6.20	7.80
4	伸度	(%)	14.0	15.1	15.4	15.4	21.8
5	中間伸度	(%)	4.0	4.1	3.8	5.0	9.1
6	乾熱収縮率	(%)	4.2	2.8	2.2	6.1	5.5
7	接着性	(kg)	20.3	22.1	21.5	21.0	21.1
8	耐熱接着性	(kg)	15.4	20.1	20.7	12.3	20.7
9	ゴム中耐熱性	(%)	83.8	98.9	99.2	50.1	98.2
10	GY疲労寿命	(分)	42	226	254	106	423
11	GD疲労	(%)	38.6	76.5	79.8	80.2	82.5

1. Denier (d); 2. Force (kg); 3. Strength (g/d); 4. Elongation (%); 5. Intermediate elongation (%) ; 6. Dry heat shrinkage (%) ; 7. Adhesion property (Kg) ; 8. Heat resistant adhesion (Kg) ; 9. In-rubber heat resistance (%) ; 10. GY fatigue life (min.) ; 11. GD fatigue life (%)

The rubber hose reinforcing cord which is due to this invention has higher modulus and dimensional stability than the existing polyester fiber cord ; also, in comparison to the existing polyester fiber cord, it shows to be a high strength cord with much improved in-rubber heat resistance, heat resistant adhesion and fatigue resistance.

Furthermore,, the rubber hose reinforcing cord which is due to this invention, compared to the existing nylon fiber cord, has much improved modulus and dimensional stability.

[Effectiveness of the Invention]

The rubber hose reinforcing cord which is due to this invention has higher modulus and improved dimensional stability compared to the existing polyester. Also, compared to the rubber hose in which the reinforcing cord made of the existing polyester is buried, the cord buried in the rubber hose which is due to this invention has much improved in-rubbber heat ressitance, adhesion property, particularly the heat resistant adhesion after high temperature history and fatigue resistance and, as the mresult, it has very good durability against the repeated fatigue such as the pressure fluctuation in the rubber hose.

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